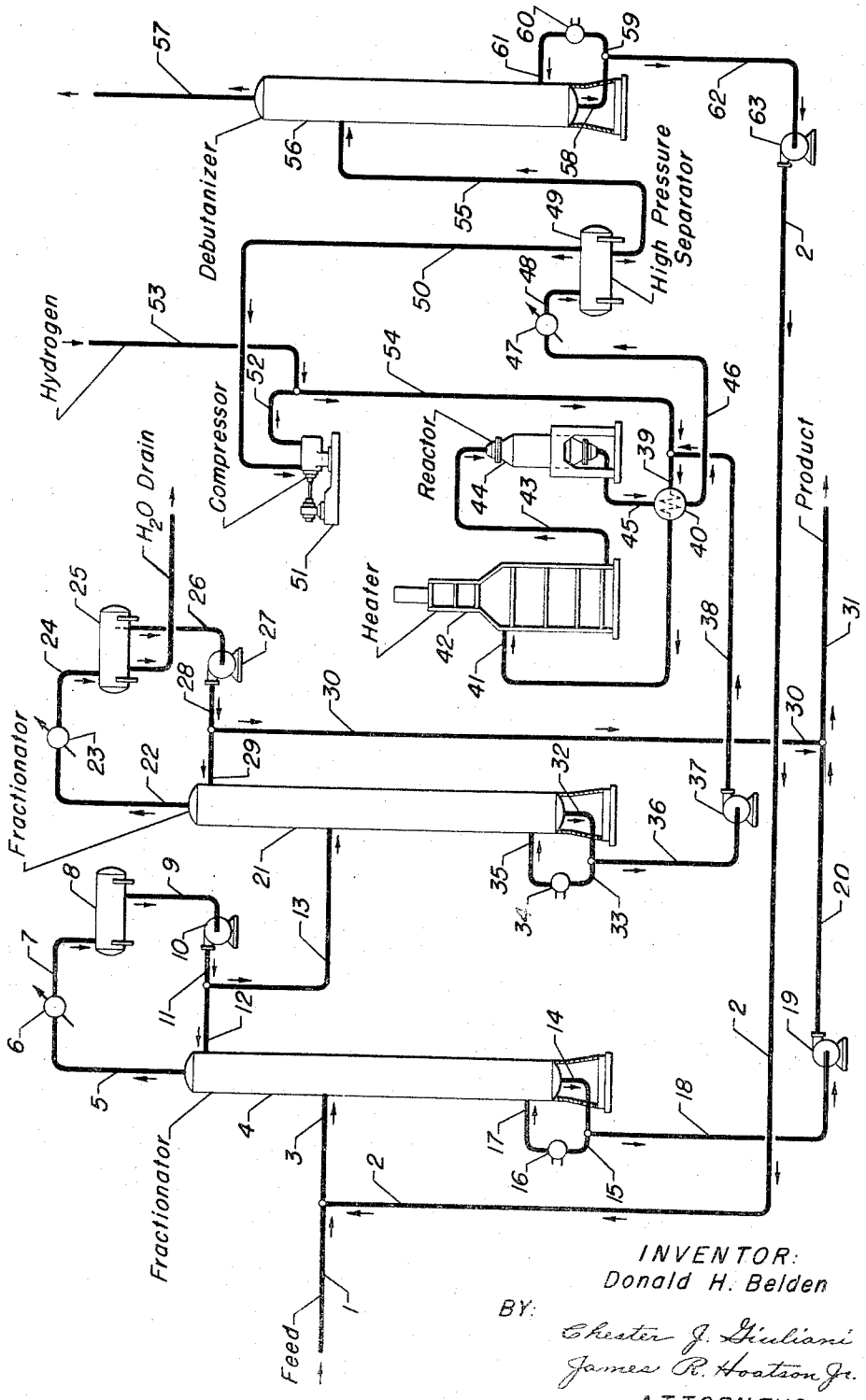
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ISOMERIZATION OF SATURATED HYDROCARBONS

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ISOMERIZATION OF SATURATED HYDROCARBONS

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The invention relates to the isomerization of saturated hydrocarbons in the presence of an isomerization catalyst. More particularly, this invention relates to the isomerization of paraffinic hydrocarbons in a unitary process comprising selective fractionation, isomerization, and recycle. Still more particularly, this invention relates to the vapor phase isomerization of paraffinic hydrocarbons boiling above butanes and pentanes in which process high yields of high antiknock hydrocarbon fractions are produced with minimum loss to byproducts such as dry gas and high boiling materials. Simultaneously with the maximum utilization of available relatively straight chain paraffinic hydrocarbons, this invention relates to a particular series of process steps, the use of which result in maximum catalyst life and optimum product quality. This invention is particularly directed to an improved process for the production of dimethylbutanes by the isomerization of relatively straight chain hexane hydrocarbons. These objectives are accomplished by the unique combination process of the present invention as will be set forth hereinafter.

Production of highly branched chain paraffinic hydrocarbons having high antiknock properties and therefor suitable for use in automotive and aviation fuels is of considerable importance in the petroleum refining industry. Furthermore, the recent introduction of automobile engines of high compression ratio has necessitated the utilization of high antiknock fuels in these engines to obtain maximum horsepower output therefrom. Thus the demand for higher and higher octane number fuels has led to the need for increased quantities of highly branched chain paraffinic hydrocarbons for use as blending agents in gasoline. A convenient source of highly branched chain paraffinic hydrocarbons is the catalytic isomerization of less highly branched chain paraffinic hydrocarbons. n-Butane and n-pentane have been isomerized to isobutane and isopentane respectively by various prior art processes utilizing either liquid or vapor phase. However, it is well known in the prior art that cracking occurs along with isomerization, and that this cracking increases with increasing molecular weight of the hydrocarbon reactant. Thus hexane fractions have never been successfully isomerized on a commercial scale. A process for such isomerization is particularly attractive when it is realized that a hexane fraction can be converted by proper isomerization and fractionation into a pool of motor fuel having an F–1 +3 cc. octane number of over 100. It is therefore an object of this invention to provide a process which will yield these desired high octane hexane isomers.

Prior are processes for the isomerization of saturated hydrocarbons have taught the utilization of various catalytic agents to accelerate the desired molecular rearrangement at the conditions selected. Ordinarily, the catalytic agents utilized have comprised metal halides such as aluminum chloride, aluminum bromide, etc., which were activated by addition of the respective hydrogen halide thereto. These catalytic agents are very

active and effect high conversions per pass. However this high activity is accompanied by many disadvantages. One of the greatest disadvantages is the fact that these catalytic materials not only accelerate isomerization reactions, but they also induce decomposition reactions. These decomposition reactions are particularly detrimental to the overall economics of an isomerization process since they cause a loss of a portion of the charging stock as well as increasing catalyst consumption by the reaction of fragmental material with the catalytic agent to form sludge-like materials. The process of the present invention overcomes these disadvantages by utilization of more recently developed catalysts and thus the use of the process along with these catalysts results in the attainment of isomerization reactions which have hereinbefore been available to the petroleum industry.

As stated hereinabove the process of the present invention is particularly directed to the isomerization of hexane hydrocarbons. Hexane hydrocarbons boil from about 40° to about 90° C. (104–185° F.) and analyses of typical hexane fractions show that they contain varying quantities of cyclopentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, n-hexane, methylcyclopentane, dimethylpentanes, cyclohexane, and benzene. The boiling points and octane numbers of these six carbon atom hydrocarbons are given in the following table:

TABLE I

	Boiling Point		F–1 Octane No.	
	° C.	° F.	Clear	+3 cc.
2,2-dimethylbutane	49.7	121.5	92.3	104.0
2,3-dimethylbutane	58.0	136.4	103.5	>120
2-methylpentane	60.3	140.5	73.4	93.1
3-methylpentane	63.3	145.9	74.5	93.4
n-hexane	68.7	155.7	25.0	65.3
methylcyclopentane	71.8	161.3	92.0	103.1
benzene	80.1	176.2	>120	>120
cyclohexane	80.7	177.3	84.0	97.4

By the process of this invention the high octane number components are not passed to the isomerization reactor but are fractionated from the fresh feed. Such components include the 2,2-dimethylbutane, 2,3-dimethylbutane, methylcyclopentane, benzene, and cyclohexane. When processing hexanes in the process of this invention, the reaction zone feed will comprise 2-methylpentane, 3-methylpentane, and n-hexane. This reaction zone feed will be converted therein to an equilibrium mixture of hexane isomers including the dimethylbutane compounds. In this manner a total gasoline pool having an F–1+3 cc. octane number of greater than 100 is produced.

In one embodiment the present invention relates to a process for the isomerization of an isomerizable saturated hydrocarbon fraction, characterized by an average molecular weight greater than about 80, to produce a composite hydrocarbon fraction having an F–1+3 cc. octane number of at least 100, said isomerization being carried out in the presence of an isomerization catalyst, which comprises passing to a first fractionation zone said first mentioned hydrocarbon fraction in combination with liquid phase isomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially naphthene free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction, removing said substantially pure cyclics hydrocarbon bottoms fraction having an F—1+3 cc. octane number of at least 100 as one product from the process, passing said substantially naphthene free overhead hydrocarbon fraction from said first fractionation zone to a second frac-

tionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead fraction characterized by a major proportion of hydrocarbons with at least two methyl substituents per molecule and an F–1+3 cc. octane number of at least 100 and to produce a bottoms hydrocarbon fraction, removing said overhead hydrocarbon fraction as a second product from the process, passing said last mentioned bottoms hydrocarbon fraction to an isomerization zone wherein low octane number hydrocarbons are isomerized to higher octane number hydrocarbons, recycling the isomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover the high octane number hydrocarbons therefrom as product and to separate low octane number hydrocarbons as aforesaid for reuse and internal recycle in said process, and compositing the aforesaid product streams.

A specific embodiment of the invention relates to a process for the isomerization of an isomerizable hexane fraction to produce a composite hexane fraction having an F–1+3 cc. octane number of at least 100, said isomerization being carried out in the presence of hydrogen and an isomerization catalyst comprising platinum, alumina, and combined halogen, which comprises passing to a first fractionation zone said first mentioned hexane hydrocarbon fraction in combination with liquid phase isomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially naphthene free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction containing methylcyclopentane and cyclohexane, removing said cyclics hydrocarbon bottoms fraction containing methylcyclopentane and cyclohexane as one product from the process, passing said substantially naphthene free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes and n-hexane, removing said overhead hydrocarbon fraction as a second product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes and n-hexane to an isomerization zone wherein an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes is produced, recycling the isomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover dimethylbutanes therefrom as one product and to separate methylpentanes and n-hexane for reuse and internal recycle in said process, and compositing the aforesaid product streams.

The combination process of this invention has diverse advantages, all interrelated. The process prevents a buildup of heavier products in the combined feed to the reaction zone since these heavier products are eliminated by removal in the bottoms from the first fractionation zone along with methylcyclopentane and cyclohexane. In a preferred embodiment the isomerization process of the present invention is carried out in the presence of hydrogen. In the presence of hydrogen, cracking of naphthenic hydrocarbons occurs readily due to the acid function of the preferred catalysts. Thus the process of the present invention prevents destruction of C_6 naphthenic hydrocarbons by removal thereof prior to isomerization in the lower portion of the first fractionation zone. By elimination of the naphthenes from the reaction zone combined feed, conversion of methylcyclopentane to cyclohexane due to equilibrium considerations is prevented. This is a definite advantage in the overall pool octane number since methylcyclopentane has a higher octane number than cyclohexane. Benzene which is naturally occurring in many C_6 hydrocarbon fractions is hydrogenated to cyclohexane in the presence of typical catalysts utilized in this process. The benzene content of the reaction zone feed is substantially

reduced by the particular fractionation of this process. It cannot be completely eliminated due to azeotroping with paraffinic hydrocarbons. That benzene which is present in the reaction zone feed is hydrogenated, and the cyclohexane produced is isomerized to an equilibrium mixture of methylcyclopentane and cyclohexane. These naphthenes are then eliminated as set forth hereinabove upon recycle of the reaction zone effluent to the fractionation zones of the present process. By elimination of the naturally present naphthenes from the reaction zone feed, and by reduction of the benzene content of this feed, hydrogen consumption in the process is minimized. This results in an economic advantage since large quantities of hydrogen do not have to be furnished to the process. Major hydrogen consumption is that due to hydrogen solubility in the reaction zone effluent in the high pressure separator, described hereinafter. The process prevents so-called reverse isomerization of high octane number dimethylbutanes to other hexane isomers by separation of these high octane number components prior to isomerization. At any particular isomerization reaction temperature, the formation of hexane isomers is limited by the equilibrium distribution of these isomers. By having the high octane number dimethylbutanes present in the reaction zone feed, the conversion of monomethylpentanes and n-hexane to these compounds cannot proceed to the same extent as when these isomers are absent. Furthermore, the equilibrium among hexane isomers is dynamic so that the desired dimethylbutane isomers can undergo reverse isomerization if present in substantial quantities in the reaction zone feed. Another advantage of the process of the present invention is that catalyst deactivation or destruction is minimized or substantially eliminated by distillation drying of the reactor feed and rejection of small quantities of water contained therein along with the dimethylbutanes in the overhead from the second fractionation zone. Thus the reaction zone feed is a fractionation zone bottoms product and by this means full advantage is taken of maximum distillation drying. All isomerization catalysts depend upon an acid function to accomplish the desired reaction. This acid function is destroyed or decreased by contact with water. The preferred catalysts of the present invention which operate at elevated temperatures contain this acid function in relatively minor quantities, and thus are utilized at intermediate processing temperatures. Thus small amounts of water, which can be brought in with the feed stock, cause relatively rapid catalyst deactivation. Utilization of the process of the present invention prevents this deactivation. By elimination of dimethylbutanes, methylcyclopentane, and cyclohexane from the reaction zone feed, the quantity of feed is reduced as well as the combined feed ratio and thus the total investment necessary for catalyst can be substantially reduced. These and other advantages will be explained more fully in the following detailed description of the process of the present invention.

As set forth hereinabove this invention relates to a process for the isomerization of an isomerizable saturated hydrocarbon fraction characterized by an average molecular weight greater than about 80. Hydrocarbons within the scope of the above limitation and utilizable in the process of this invention include methylcyclopentane, cyclohexane, n-hexane, 2-methylpentane, 3-methylpentane, 2-methylhexane, 3-methylhexane, 3-ethylpentane, n-heptane, methylcyclohexane, ethylcyclohexane, n-octane, 2-methylheptane, 3-methylheptane, etc. As stated previously, the process of this invention is particularly applicable to the isomerization of hexane fractions. These hexane fractions may be obtained from various sources including fractionation from straight run gasoline, straight run naphtha, natural gasoline, catalytically reformed naphtha, and catalytically reformed gaso-

line. Analyses of typical hexane fractions from various crude sources are given in the following Table II:

Table II.—Analyses of typical C_6 fractions

[Fractionation cut 40-74° C. (104-165° F.).]

Composition, Vol. Percent	Barninus Crude	Pennsylvania	South Louisiana	Gulf Coast	Oklahoma	Wyoming	Arabian	Nat'l Gasol Texas	Nat'l Gasol Texas
Cyclopentane	5	2	2	3	3	4	2	2	5
2,2-dimethylbutane	Tr	3	2	3	1	1	1	2	3
2,3-dimethylbutane	5	5	5	5	2	3	3	4	6
2-methylpentane	20	27	25	25	22	22	22	28	28
3-methylpentane	19	18	18	20	15	14	16	17	15
n-Hexane	32	36	31	30	40	35	44	34	23
Methylcyclopentane	16	6	14	3	14	18	7	9	14
Dimethylpentanes	Tr	Tr	1	1	----------	1	1	Tr	Tr
Cyclohexane	1	Tr	1	7	1	1	2	1	2
Benzene	2	2	1	3	2	1	2	3	4
Total	100	100	100	100	100	100	100	100	100
C_6 Cyclics	19	8	16	13	17	20	11	13	20
Octane No. F-1 +3 cc	88	86	88	90	85	86	82	86	92

A detailed description of the processing of one of these hexane hydrocarbon fractions by the process of the present invention will be given hereinafter.

Various isomerization catalysts are utilizable within the generally broad scope of the process of the present invention. These catalysts include a support, an acid-acting function, and a hydrogenation component. The support may be selected from diverse refractory oxides including silicia, alumina, silica-alumina, silica-alumina-magnesia, silica-alumina-zirconia, silica-zirconia, etc. Depending upon the method of preparation and upon the treatment of the support thereafter, these various supports will have surface areas ranging from about 25 to about 500 square meters per gram. In some of these supports the acid-acting function is inherently present, as when silica-alumina is used as the support. The amount of effectiveness of this acid-acting function is then controlled by the quantity of silica which is combined with the alumina, and by the treatment of the silica-alumina, particularly by calcination, prior to or after compositing the hydrogenation component therewith. Of the various supports, alumina is preferred, and particularly gamma-alumina having a surface area of from about 150 to about 450 square meters per gram. When gamma-alumina is utilized as the support, the acid-acting function can be added to the catalyst by the incorporation therein of what is known in the art as combined halogen. The amount of combined halogen can be varied from about 0.01 to about 8% by weight based on the alumina. Of the various halogens which may be utilized, both fluorine and chlorine can be used satisfactorily. Thus in an alumina type catalyst to be utilized at reaction temperatures of from 750° to about 850° F., about 0.3% by weight of fluorine and about 0.3% by weight of chlorine may be incorporated therein. When it is desirable to utilize the catalyst at lower temperatures, for example, from about 500° to about 750° F., as is the case in the preferred embodiment of the present invention, the combined halogen which will be utilized along with the alumina support is fluorine, and this fluorine will be utilized in an amount of from about 2.5% to about 4.5% by weight. The composite will then have the desired hydrogenation component combined therewith. This hydrogenation component will normally be selected from groups VI(B) and VIII of the periodic table or mixtures thereof. Such hydrogenation components include chromium, molybdenum, tungsten, iron, cobalt, nickel, and the so-called platinum group metals including platinum, palladium, ruthenium, rhodium, osmium, and iridium. Of the various hydrogenation components which may be utilized, those of the platinum group metals are preferred, and of these platinum group metals, platinum itself is particularly preferred. The hydrogenation component of the catalysts of the present invention will normally be utilized in an amount of from about 0.01% to about 10% by weight based on the weight of the support. With the preferred platinum group metals, particularly platinum, the quantity utilized will range from about 0.01% to about 2% by weight. A particularly preferred catalyst comprising platinum, combined halogen, and alumina will contain 0.4% platinum, 4.0% fluorine, and alumina. Because of equilibrium considerations and because it is often desirable and/or advisable to carry out the isomerization reaction at the lowest possible temperature, for example, from about 300° to about 500° F., catalysts may also be prepared by impregnating composites such as described hereinabove with a metal halide of the Friedel-Crafts type. For example, an excellent low temperature isomerization catalyst can be prepared by impregnating from about 5 to about 20% aluminum chloride onto a composite of platinum, alumina, and combined halogen.

The isomerization process of the present invention can be carried out at varying conditions of temperature, pressure, space velocity, and combined feed ratio. The temperature utilized will generally be dictated by the particular catalyst selected. Thus the temperature may range over a wide range of from about 300° to about 800° F. The pressure will be selected so as to insure vapor phase operation and depending upon the particular temperature utilized will range from about 100 to about 1000 pounds per square inch or more. Liquid hourly space velocity will range from about 0.1 to about 10 or more, the only limitation being that equilibrium mixtures of isomerized hydrocarbons or a close approach thereto shall be obtained in the reaction zone effluent. The combined feed ratio which is defined as the total amount of fresh feed entering the reactor and recycle divided by the quantity of fresh feed will range from 1 up to about 5 or more. Values in between these two limits are determined by the concentration of the desired high octane number hydrocarbons in the reaction zone effluent. In the preferred embodiment of the present invention, hydrogen is utilized to minimize cracking and to maintain the surface of the catalyst in a carbon free condition. The quantity of hydrogen utilized will range from about 0.25 to about 10 mols or more of hydrogen per mol of hydrocarbon. Hydrogen consumption will be exceedingly small, in the range of from about 30 to about 100 cubic feet per barrel of hydrocarbon feed.

The process of the present invention can perhaps be best understood by reference to the accompanying drawing which is a schematic diagram of the process flow.

Referring to the drawing, a saturated hydrocarbon fraction characterized by an average molecular weight greater than about 80, for example, a hexane fraction separated from a straight run or catalytically reformed naphtha, is passed, as a liquid under pressure, through lines 1 and 3 to the upper portion of fractionator 4. The hydrocarbon fraction passing through lines 1 and 3 is combined in line 1 with recycle reaction zone effluent from line 2 as hereinafter set forth. The combined

feed to fractionator 4 is fractionated therein to separate a substantially naphthene free overhead from high octane number naphthenes which occur in the feed or which may be produced during processing by hydrogenation of aromatic hydrocarbons. Ordinarily, these naphthenic hydrocarbons occur in the feed and their destruction via hydrocracking is prevented by removal at this point. Furthermore, at certain temperatures of operation methylcyclopentane is isomerized to cyclohexane. This is undesirable since methylcyclopentane normally occurs in larger quantities than does cyclohexane, and since methylcyclopentane has a higher octane number than does cyclohexane. Thus the hydrocarbon stream from line 3 is fractionated in fractionator 4 and the substantially naphthene free portion thereof separated overhead. This naphthene free hydrocarbon fraction passes through line 5, is condensed in condenser 6, and passes through line 7 into receiver 8. The substantially naphthene free hydrocarbons from receiver 8 are withdrawn therefrom through line 9 by pump 10 which discharges into line 11 and supplies reflux to fractionation zone 4 by means of line 12. The net substantially naphthene free hydrocarbon stream from fractionation zone 4 passes from line 11 through line 13 to fractionation zone 21 as hereinafter described.

Fractionation zone 4 is heated by reboiling a portion of the higher boiling hydrocarbons which are withdrawn through lines 14 and 15, and are passed through heat exchanger 16. The heated hydrocarbons are then returned to a lower portion of fractionation zone 4 through line 17. The higher boiling substantially pure cyclics hydrocarbon bottoms fraction having an F–1+3 cc. octane number of at least 100 is withdrawn from the bottom of fractionation zone 4 through lines 14 and 18, and is pumped by pump 19 through line 20 for combination with the other high octane number fraction hereinafter described.

The purpose of fractionation zone 21 is to fractionate the feed thereto to produce a hydrocarbon fraction characterized by a major proportion of the hydrocarbons with at least two methyl substituents per molecule and and F–1+3 cc. octane number of at least 100 and to produce reaction zone feed. The overhead product from this fractionation zone 21 thus comprises dimethylalkanes naturally occurring in the feed and dimethylalkanes from the reaction zone effluent which have been formed as a result of the isomerization of n-paraffins and monomethylalkanes as set forth hereinafter. For example, when processing a hexane fraction, the overhead product which is separated from the process at this point comprises 2,2- and 2,3-dimethylbutanes naturally occurring in the feed and 2,2- and 2,3-dimethylbutanes from the reaction zone effluent which have been formed as a result of the isomerization of n-hexane and 2- and 3-methylpentanes as set forth hereinafter. Also, any water which is dissolved in the feed or produced during the processing separates overhead at this point due to distillation drying. Thus the bottoms from fractionation zone 21 which pass to the reaction zone are for all practical purposes substantially water free. The above described high octane number dimethylalkane hydrocarbon stream passes from fractionator 21 overhead through line 22, is condensed in condenser 23, and passes through line 24 to receiver 25. From receiver 25, the hydrocarbon fraction passes through line 26 to pump 27 and into line 28 which provides reflux for fractionator 21 by means of line 29. The net dimethylparaffin hydrocarbon stream is withdrawn through line 30 and is combined with the other high octane number fraction hereinabove described and both fractions are then withdrawn through line 31.

Fractionator 21 is heated by reboiling a portion of the higher boiling hydrocarbons, which are withdrawn through lines 32 and 33 and passed through heat exchanger 34 and the heated hydrocarbons are then returned into a lower portion of fractionation zone 21 through line 35. The higher boiling saturated hydrocarbons, substantially free from naphthenes, as hereinabove described, and substantially free from dimethylalkane hydrocarbons, are withdrawn from fractionation zone 21 through lines 32 and 36 by pump 37.

The net hydrocarbon stream from fractionator 21 is pumped by pump 37 through line 38 and line 39. From line 39 this hydrocarbon stream is heat exchanged with the hot reaction zone effluent in heat exchanger 40 and then passes through line 41 to heater 42. In heater 42, the stream is heated to the desired reaction temperature, and then passes through line 43 to reaction zone 44. It is in this reaction zone 44 that the less highly branched chain and straight chain hydrocarbons are isomerized to an equilibrium mixture of saturated hydrocarbon isomers. As will be set forth hereinafter, the hydrocarbons are processed in the presence of hydrogen which is introduced via lines 52 and 54 into line 39. This hydrogen also hydrogenates any aromatic hydrocarbons in reaction zone 44 and the thus produced naphthenic hydrocarbons are then isomerized to an equilibrium mixture of the same during isomerization of the remaining saturated hydrocarbons.

As stated hereinabove, the conditions utilized in reaction zone 42 will depend upon the particular isomerization catalyst utilized therein. It was pointed out above that a preferred catalyst in the process of this invention is one comprising a platinum group metal, particularly platinum, combined halogen, and alumina. With such a catalyst, the pressure utilized in the reaction zone will range from about 100 to about 1000 pounds per square inch, the temperature will range from about 300° to about 800° F., and the hourly liquid space velocity will range from about 0.1 to about 10. The hydrogen to hydrocarbon ratio in the reaction zone will range from about 0.25 to about 10 mols of hydrogen per mol of hydrocarbons. When the catalyst utilized comprises platinum, alumina, and combined fluorine in an amount of from about 2.5 to about 4.5 weight percent of the latter, the reaction temperature will be lower than the higher part of the above set forth range, for example, from about 500° to about 750° F. When the catalyst comprises platinum, alumina, and combined halogen onto which has been impregnated a metal halide of the Friedel-Crafts type, such as aluminum chloride, the temperature will still be lower, for example, from about 300° to about 500° F. In some instances it is desirable and/or advisable to utilize hydrogen halide along with these catalysts and thus the use of hydrogen chloride, for example, is within the generally broad scope of the present invention.

The reaction zone effluent passes from reactor 44 through line 45 in indirect heat exchange with the reaction zone feed through heat exchanger 40 and then passes through line 46, is cooled in condenser 47, and passes through line 48 to high pressure separator 49. The high pressure separator 49 is utilized for separating hydrogen from the reaction zone effluent, which hydrogen is separated and passed through line 50 to compressor 51 where its pressure is increased to the desired number of pounds per square inch, and then the hydrogen is discharged through lines 52 and 54 described hereinabove. When a hydrogen halide is utilized along with the hereinabove described catalyst as a catalyst promoter, it will pass through line 50 to compressor 51 as hereinabove described. Hydrogen and/or hydrogen halide for startup and makeup are added through line 53.

The cooled reaction zone effluent after high pressure separation is discharged from separator 49 through line 55 to debutanizer 56. This debutanizer is a conventional fractionation zone by means of which a light hydrocarbon gas or low boiling cracked products and dissolved H_2 is removed from the process. This removal is accomplished through line 57 which will include re-

ceiver and reflux means not shown. Debutanizer 56 is heated by passing a portion of the higher boiling hydrocarbons through lines 58 and 59 to heat exchanger 60 from which the heated hydrocarbons are discharged into a lower portion of the debutanizer via line 61. The net reaction zone effluent is withdrawn from debutanizer 56 through lines 58 and 62 by means of pump 63 which discharges the liquid reaction zone effluent through line 2 to fractionator 4 for fractionation as described hereinabove.

EXAMPLE I

One specific example of the operation of the process with a platinum-alumina-combined halogen catalyst and as the process is carried out similar to that set forth hereinabove with reference to the drawing is described herewith now in connection with the drawing. The catalyst utilized comprises alumina containing 0.4% platinum and about 0.5% combined halogen. The combined halogen comprises about 0.3% fluorine and about 0.2% chlorine.

This example illustrates the isomerization of a Gulf Coast hexane fraction, boiling point 40–74° C. The composition of the Gulf Coast hexane fraction is as follows: cyclopentane, 3%, 2,2-dimethylbutane, 3%; 2,3-dimethylbutane, 5%; 2-methylpentane, 25%; 3-methylpentane, 20%; n-hexane, 30%; methylcyclopentane, 3%; dimethylpentanes, 1%; cyclohexane, 7%; and benzene, 3%. Referring again to the drawing this hexane fraction having an average molecular weight greater than 80 in the quantity of 1000 barrels per day is passed as a liquid under pressure through line 1 and through line 3 to an upper portion of fractionator 4. This fresh feed stream has combined therewith in line 1, 3830 barrels per day of recycle reaction zone effluent from line 2 as hereinafter described. This recycle hexane stream consisting of the liquid reaction zone effluent contains 452 barrels per day of 2,2-dimethylbutane, 298 barrels per day of 2,3-dimethylbutane, 1310 barrels per day of 2-methylpentane, 862 barrels per day of 3-methylpentane, and 908 barrels per day of n-hexane. Thus the total combined feed to fractionator 4 amounts to 4830 barrels per day comprising 30 barrels per day of cyclopentane, 482 barrels per day of 2,2-dimethylbutane, 348 barrels per day of 2,3-dimethylbutane, 1560 barrels per day of 2-methylpentane, 1062 barrels per day of 3-methylpentane, 1208 barrels per day of n-hexane, 30 barrels per day of methylcyclopentane, 10 barrels per day of dimethylpentane, 70 barrels per day of cyclohexane, and 30 barrels per day of benzene. The combined feed to fractionator 4 is fractionated therein under a 4:1 molal reflux to feed ratio and a substantially naphthene free stream is separated overhead therefrom in an amount of 4690 barrels per day. This 4690 barrels per day contains 30 barrels per day of cyclopentane, 482 barrels per day of 2,2-dimethylbutane, 348 barrels per day of 2,3-dimethylbutane, 1560 barrels per day of 2-methylpentane, 1062 barrels per day of 3-methylpentane, and 1208 barrels per day of n-hexane. This fractionator 4 overhead is withdrawn therefrom through line 5, is condensed in cooler 6, and is passed through line 7 to receiver 8. From receiver 8 the liquid is withdrawn through line 9 by pump 10 and supplies feed to fractionator 21, described hereinafter, via line 13.

Fractionator 4 bottoms are withdrawn from line 14 through line 18 and have a compositon as follows: 30 barrels per day of methylcyclopentane, 10 barrels per day of dimethylpentanes, 70 barrels per day of cyclohexane, and 30 barrels per day of benzene. The F–1+3 cc. octane number of this stream is 103.7. These bottoms are then pumped by pump 19 through lines 20 and 31 to storage.

The feed stream to fractionation zone 21 in the quantity of 4690 barrels per day and of the composition described hereinabove is fractionated therein under a 4:1 molal reflux to feed ratio and the overhead passed therefrom through line 22, condensed in cooler 23, and passed as a liquid through line 24 to receiver 25. Fractionation zone 21 separates a substantially monomethylpentane and n-hexane free dimethylbutane stream overhead therefrom in an amount of 860 barrels per day. This 860 barrels per day contains 30 barrels per day of cyclopentane, 482 barrels per day of 2,2-dimethylbutane, and 348 barrels per day of 2,3-dimethylbutane. This stream has an F–1+3 cc. octane number of 112.0. This fractionator overhead is withdrawn from receiver 25 through line 26 by pump 27 and the net product is pumped through lines 30 and 31 to storage. In storage this stream with its F–1+3 cc. octane number of 112.0 is blended with the aforementioned bottoms stream from fractionator 4, said latter stream having an F–1+3 cc. octane number of 103.7, the combined pool thus having an F–1+3 cc. octane number of greater than 100.

The substantially dimethylbutane free bottoms stream from fractionator 21 in the quantity of 3830 barrels per day is the reactor feed. The composition of this stream is as follows: 1560 barrels per day of 2-methylpentane, 1062 barrels per day of 3-methylpentane, 1208 barrels per day of n-hexane. This bottoms stream is pumped by pump 37 through lines 38 and 39, where it is joined with hydrogen from line 54, through heat exchange zone 40, and line 41 to heater 42. The quantity of hydrogen which is continuously supplied is sufficient to maintain a hydrogen to hydrocarbon mol ratio of 2:1 in the reaction zone. This is accomplished by recycling hydrogen from the high pressure separator back to the reaction zone. A small quantity of substantially pure makeup hydrogen is added through line 53 to make up for the hydrogen consumed in the reaction and for that which is dissolved in the separator liquid effluent. By means of heat exchanger 40 and heater 42, the combined feed to the reaction zone is heated to a temperature of 800° F. The reaction is carried out at a pressure of about 500 p.s.i.g. in vapor phase at a liquid hourly space velocity of about 2.0. As set forth hereinabove, isomerization of the reaction zone feed is accomplished in reaction zone 44 in the presence of the hereinabove described catalyst and results in the production of 3830 barrels per day of reaction zone effluent containing 452 barrels per day of 2,2-dimethylbutane, 298 barrels per day of 2,3-dimethylbutane, 1310 barrels per day of 2-methylpentane, 862 barrels per day of 3-methylpentane, and 908 barrels per day of n-hexane.

The reaction zone effluent after heat exchange with incoming reaction zone feed is passed via lines 45 and 46 to condenser 47, and the liquid product and hydrogen gas are then passed through line 48 to high pressure separator 49. The hydrogen gas and minor amounts of low boiling hydrocarbons formed by cracking in the reaction zone are separated in high pressure separator 49 and passed through line 50 to compressor 51. High pressure separator liquid which discharges through line 55 is passed to debutanizer 56 to further separate this small amount of cracked products produced during isomerization and to prepare the liquid recycle stream as hereinabove set forth. The liquid recycle stream passes from debutanizer 56 through lines 58 and 62 to pump 63 wherein it is recycled to fractionation zone 4 via line 2.

In the above example, the small amount of cracking which is observed during processing has not been taken into account. This is due to the fact that liquid volume yields based on the feed are in the order of 98 volume percent or higher. As stated hereinabove, the F–1+3 cc. octane number of the dimethylbutane fraction is 112.0 and the F–1+3 cc. octane number of the cyclics fraction is 103.7, resulting in a pool F–1+3 cc. octane number of greater than 100.

EXAMPLE II

Another specific example of the operation of the process with a platinum-alumina-combined halogen catalyst and as the process is carried out similar to that set forth

hereinabove with reference to the drawing is described again herewith in connection with the drawing. The catalyst utilized comprises alumina containing 0.4% platinum and about 4.0% combined fluorine.

This example illustrates the isomerization of the Gulf Coast hexane fraction of the first specific example. This hexane fraction in the quantity of 1000 barrels per day is passed as a liquid under pressure through line 1 and through line 3 to an upper portion of fractionator 4. This 1000 barrels per day is made up of 30 barrels per day of cyclopentane, 30 barrels per day of 2,2-dimethylbutane, 50 barrels per day of 2,3-dimethylbutane, 250 barrels per day of 2-methylpentane, 200 barrels per day of 3-methylpentane, 300 barrels per day of n-hexane, 30 barrels per day of methylcyclopentane, 10 barrels per day of dimethylpentanes, 70 barrels per day of cyclohexane, and 30 barrels per day of benzene. This fresh feed stream has combined therewith in line 1, 3290 barrels per day of recycle reaction zone effluent from line 2 as hereinafter described. This recycle hexane stream consisting of liquid reaction zone effluent contains 494 barrels per day of 2,2-dimethylbutane, 257 barrels per day of 2,3-dimethylbutane, 1085 barrels per day of 2-methylpentane, 727 barrels per day of 3-methylpentane, and 727 barrels per day of n-hexane. Thus the total combined feed to fractionator 4 amounts to 4290 barrels per day consisting of 30 barrels per day of cyclopentane, 524 barrels per day of 2,2-dimethylbutane, 307 barrels per day of 2,3-dimethylbutane, 1335 barrels per day of 2-methylpentane, 927 barrels per day of 3-methylpentane, 1027 barrels per day of n-hexane, 30 barrels per day of methylcyclopentane, 10 barrels per day of dimethylpentanes, 70 barrels per day of cyclohexane, and 30 barrels per day of benzene. The combined feed to fractionator 4 is fractionated therein under a 4:1 molal reflux to feed ratio and a substantially naphthene free stream is separated overhead therefrom in an amount of 4150 barrels per day. This 4150 barrels per day contains 30 barrels per day of cyclopentane, 524 barrels per day of 2,2-dimethylbutane, 307 barrels per day of 2,3-dimethylbutane, 1335 barrels per day of 2-methylpentane, 927 barrels per day of 3-methylpentane, and 1027 barrels per day of n-hexane. This fractionator 4 overhead is withdrawn therefrom through line 5, is condensed in cooler 6, and is passed throuh line 7 to receiver 8. From receiver 8 the liquid is withdrawn through line 9 by pump 10 and supplies feed to fractionator 21, described hereinafter, via line 13.

Fractionator 4 bottoms are withdrawn through line 14 and through line 18 and have a composition as follows: 30 barrels per day of methylcyclopentane, 10 barrels per day of dimethylpentanes, 70 barrels per day of cyclohexane, and 30 barrels per day of benzene. The F–1+3 octane number of this stream is 103.7. These bottoms are then pumped by pump 19 through lines 20 and 31 to storage.

The feed stream to fractionation zone 21 in the quantity of 4150 barrels per day and of the composition described hereinabove is fractionated therein under a 4:1 molal reflux to feed ratio and the overhead passed therefrom through line 22, condensed in cooler 23, and passed as a liquid through line 24 to receiver 25. Fractionation zone 21 separates a substantially monomethylpentane and n-hexane free dimethylbutane stream overhead therefrom in an amount of 861 barrels per day. This 861 barrels per day contains 30 barrels per day of cyclopentane, 524 barrels per day of 2,2-dimethylbutane, and 307 barrels per day of 2,3-dimethylbutane. This stream has an F–1+3 cc. octane number of 109.8. This fractionator overhead is withdrawn from receiver 25 through line 26 by pump 27 and the net product is pumped through lines 30 and 31 to storage. In storage, this stream with its F–1+3 cc. octane number of 109.8 is blended with the aforementioned bottoms stream for fractionator 4, said latter stream having an F–1+3 cc. octane number of 103.7, the combined pool thus having an F–1+3 cc. octane number of greater than 100.

The substantially dimethylbutane free bottoms stream from fractionator 21 in the quantity of 3289 barrels per day is the reactor feed. The composition of this stream is as follows: 1335 barrels per day of 2-methylpentane, 927 barrels per day of 3-methylpentane, and 1027 barrels per day of n-hexane. This bottoms stream is pumped by pump 37 through lines 38 and 39, where it is joined with hydrogen from line 54, through heat exchange zone 40, and line 41 to heater 42. The quantity of hydrogen which is continuously supplied is sufficient to maintain a hydrogen to hydrocarbon mol ratio of 2:1 in the reaction zone. This is accomplished by recycling hydrogen from the high pressure separator back to the reaction zone. A small amount of substantially pure makeup hydrogen is added through line 53 to make up for the hydrogen consumed in the reaction and for that which is dissolved in the separator liquid effluent. By means of heat exchanger 40 and heater 42, the combined feed to the reaction zone is heated to a temperature of 600° F. The reaction is carried out at a pressure of about 400 p.s.i.g. in vapor phase at an hourly liquid space velocity of 2.0. As set forth hereinabove, isomerization of the reaction zone feed is accomplished in reaction zone 44 in the presence of the hereinabove described catalyst and results in the production of 3289 barrels per day of reaction zone effluent containing 494 barrels per day of 2,2-dimethylbutane, 257 barrels per day of 2,3-dimethylbutane, 1085 barrels per day of 2-methylpentane, 727 barrels per day of 3-methylpentane, and 727 barrels per day of n-hexane.

The reaction zone effluent after heat exchange with the incoming reaction zone feed is passed via lines 45 and 46 to condenser 47, and the liquid product and hydrogen gas are then passed through line 48 to high pressure separator 49. The hydrogen gas and minor amounts of low boiling hydrocarbons formed by cracking in the reaction ozone are separated in high pressure separator 49 and passed through line 50 to compressor 51. High pressure separator liquid which discharges through line 55 is passed to debutanizer 56 to further separate the small amount of unreacted products produced during isomerization and to prepare the liquid recycle stream as hereinabove set forth. The liquid recycle stream passes from debutanizer 56 through lines 58 and 62 to pump 63 wherein it is recycled to fractionation zone 4 via line 2.

In this second example, as previously, the small amount of cracking which is observed during processing has not been taken into account. Here again the liquid volume yields based on the feed are in the order of 98 volume percent or higher. As stated, the F–1+3 cc. octane number of the dimethylbutane fraction is 109.8 and the F–1+3 cc. octane number of the cyclics fraction is 103.7, resulting in a pool F–1+3 cc. octane number of greater than 100.

EXAMPLE III

A still further specific example of the operation of the process with a platinum-alumina-combined halogen catalyst containing aluminum chloride and as the process is carried out similar to that set forth hereinabove with reference to the drawing is described herewith. The catalyst utilized comprises alumina containing 0.4% platinum, about 0.3% fluorine, and about 0.2% chlorine, said composite having been impregnated with about 17% by weight of aluminum chloride.

In this example the same Gulf Coast hexane fraction is isomerized. Referring again to the drawing, this hexane fraction having an average molecular weight greater than 80 in the quantity of 1000 barrels per day is passed as a liquid under pressure through line 1 and through line 3 to an upper portion of fractionation zone 4. This 1000 barrels per day of Gulf Coast hexane fraction contains 30 barrels per day of cyclopentane, 30 barrels per

day of 2,2-dimethylbutane, 50 barrels per day of 2,3-dimethylbutane, 250 barrels per day of 2-methylpentane, 200 barrels per day of 3-methylpentane, 300 barrels per day of n-hexane, 30 barrels per day of methylcyclopentane, 10 barrels per day of dimethylpentanes, 70 barrels per day of cyclohexane, and 30 barrels per day of benzene. This feed stream has combined therewith in line 1, 2400 barrels per day of recycle reaction zone effluent from line 2 as hereinafter described. This recycle hexane stream consisting of the liquid reaction zone effluent contains 495 barrels per day of 2,2-dimethylbutane, 254 barrels per day of 2,3-dimethylbutane, 818 barrels per day of 2-methylpentane, 475 barrels per day of 3-methylpentane, and 358 barrels per day of n-hexane. Thus the total combined feed to fractionator 4 amounts to 3400 barrels per day comprising 30 barrels per day of cyclopentane, 525 barrels per day of 2,2-dimethylbutane, 304 barrels per day of 2,3-dimethylbutane, 1068 barrels per day of 2-methylpentane, 675 barrels per day of 3-methylpentane, 658 barrels per day of n-hexane, 30 barrels per day of methylcyclopentane, 10 barrels per day of dimethylpentanes, 70 barrels per day of cyclohexane, and 30 barrels per day of benzene. The combined feed to fractionator 4 is fractionated therein under a 4:1 molal reflux to feed ratio and a substantially naphthene free stream is separated overhead therefrom in an amount of 3260 barrels per day. This 3260 barrels per day contains 30 barrels per day of cyclopentane, 525 barrels per day of 2,2-dimethylbutane, 304 barrels per day of 2,3-dimethylbutane, 1068 barrels per day of 2-methylpentane, 675 barrels per day of 3-methylpentane, and 658 barrels per day of n-hexane. This fractionator 4 overhead is withdrawn therefrom through line 5, is condensed in cooler 6, and is passed through line 7 to receiver 8. From receiver 8 the liquid is withdrawn through line 9 by pump 10 and supplies feed to fractionator 21, described hereinafter, via line 13.

Fractionator 4 bottoms are withdrawn from line 14 through line 18 and have a composition as follows: 30 barrels per day of methylcyclopentane, 10 barrels per day of dimethylpentanes, 70 barrels per day of cyclohexane, and 30 barrels per day of benzene. The F–1+3 cc. octane number of this stream is 103.7. These bottoms are then pumped by pump 19 through lines 20 and 31 to storage.

The feed stream to fractionation zone 21 in the quantity of 3260 barrels per day and of the composition described hereinabove is fractionated therein under a 4:1 molal reflux to feed ratio and the overhead passes therefrom through line 22, condensed in cooler 23, and passed as a liquid through line 24 to receiver 25. Fractionation zone 21 separates a substantially monomethylpentane and n-hexane free dimethylbutane stream overhead therefrom in an amount of 859 barrels per day. This 859 barrels per day contains 30 barrels per day of cyclopentane, 525 barrels per day of 2,2-dimethylbutane, and 304 barrels per day of 2,3-dimethylbutane. This stream has an F–1+3 cc. octane number of 109.8. This fractionator overhead is withdrawn from receiver 25 through line 26 by pump 27 and the net product is pumped through lines 30 and 31 to storage. In storage this stream with its F–1+3 cc. octane number of 109.8 is blended with the aforementioned bottoms stream from fractionator 4, said latter stream having an F–1+3 cc. octane number of 103.7, the combined pool thus having an F–1+3 cc. octane number greater than 100.

The substantially dimethylbutane free bottoms stream from fractionator 21 in the quantity of 2401 barrels per day is the reactor feed. The composition of this stream is as follows: 1068 barrels per day of 2-methylpentane, 675 barrels per day of 3-methylpentane, and 658 barrels per day of n-hexane. This bottoms stream is pumped by pump 37 through lines 38 and 39, where it is joined with hydrogen from line 54, through heat exchange zone

40 and line 41 to heater 42. The quantity of hydrogen which is continuously supplied is sufficient to maintain a hydrogen to hydrocarbon mol ratio of 1:1 in the reaction zone. This is accomplished by recycling hydrogen from the high pressure separator to the reaction zone. A small amount of substantially pure makeup hydrogen is added through line 53 to make up for the hydrogen consumed in the reaction and for that which is dissolved in the separator liquid effluent. By means of heat exchanger 40 and heater 42, the combined feed to the reaction zone is heated to a temperature of 350° F. The reaction is carried out at a pressure of about 300 p.s.i.g. in vapor phase at an hourly liquid space velocity of 0.5. As set forth hereinabove, isomerization of the reaction zone feed is accomplished in reaction zone 44 in the presence of the hereinabove described catalyst and results in the production of 2400 barrels per day of reaction zone effluent containing 495 barrels per day of 2,2-dimethylbutane, 254 barrels per day of 2,3-dimethylbutane, 818 barrels per day of 2-methylpentane, 475 barrels per day of 3-methylpentane, and 358 barrels per day of n-hexane.

The reaction zone effluent after heat exchange with incoming reaction zone feed is passed via lines 45 and 46 to condenser 47, and the liquid product and hydrogen gas are then passed through line 48 to high pressure separator 49. The hydrogen gas and minor amounts of low boiling hydrocarbons formed by cracking in the reaction zone are separated in high pressure separator 49 and passed through line 50 to compressor 51. High pressure separator liquid which discharges through line 55 is passed to debutanizer 56 to further separate the small amount of cracked products produced during isomerization and to prepare the liquid recycle stream as hereinabove set forth. The liquid recycle stream passes from debutanizer 56 through lines 58 and 62 to pump 63 wherein it is recycled to fractionation zone 4 via line 2.

In the above example the small amount of cracking which is observed during processing has not been taken into account. Here again, the liquid volume yields based on the feed are in the order of 98 volume percent or higher. As stated hereinabove, the F–1+3 cc. octane number of the dimethylbutane fraction is 109.8 and the F–1+3 cc. octane number of the cyclics fraction is 103.7, resulting in a pool F–1+3 cc. octane number of greater than 100.

I claim as my invention:

1. A process for the isomerization of an isomerizable saturated hydrocarbon fraction, characterized by an average molecular weight greater than about 80, to produce a composite hydrocarbon fraction having an F–1+3 cc. octane number of at least 100, said isomerization being carried out in the presence of an isomerization catalyst, which comprises passing to a first fractionation zone said first mentioned hydrocarbon fraction in combination with liquid phase isomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially naphthene-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction, removing said substantially pure cyclics hydrocarbon bottoms fraction having an F–1+3 cc. octane number of at least 100 as one product from the process, passing said substantially naphthene-free overhead hydrocarbon fraction from said first fractionation zone to a second fractionation zone as freed therefor, fractionating said hydrocarbons to produce an overhead fraction characterized by a major proportion of hydrocarbons with at least two methyl substituents per molecule and an F–1+3 cc. octane number of at least 100 and to produce a bottoms hydrocarbon fraction, removing said overhead hydrocarbon fraction as a second product from the process, passing said last mentioned bottoms hydrocarbon fraction to an isomerization zone wherein low octane number hydrocarbons are

isomerized to higher octane number hydrocarbons, recycling the isomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover the high octane number hydrocarbons therefrom as product and to separate low octane number hydrocarbons as aforesaid for reuse and internal recycle in said process, blending said second product with said cyclics hydrocarbon bottoms fraction and recovering the resultant blend as said composite fraction.

2. A process for the isomerization of an isomerizable hexane hydrocarbon fraction to produce a composite hexane hydrocarbon fraction having an F–1+3 cc. octane number of at least 100, said isomerization being carried out in the presence of hydrogen and isomerization catalyst comprising platinum, alumina, and combined halogen, which comprises passing to a first fractionation zone said first mentioned hexane hydrocarbon fraction in combination with liquid phase isomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially naphthene-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction containing methylcyclopentane and cyclohexane, removing said cyclics hydrocarbon bottoms fraction containing methylcyclopentane and cyclohexane as one product from the process, passing said substantially naphthene-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes and n-hexane, removing said overhead hydrocarbon fraction as a second product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes and n-hexane to an isomerization zone wherein an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes is produced, recycling the isomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover dimethylbutanes therefrom as one product and to separate methylpentanes and n-hexane as aforesaid for reuse and internal recycle in said process, blending said second product with said cyclics hydrocarbon bottoms fraction and recovering the resultant blend as said composite fraction.

3. A process for the isomerization of an isomerizable hexane hydrocarbon fraction to produce a composite hexane hydrocarbon fraction having an F–1+3 cc. octane number of at least 100, said isomerization being carried out in the presence of hydrogen and an isomerization catalyst comprising platinum, alumina, and combined halogen, which comprises passing to a first fractionation zone said first mentioned hexane hydrocarbon fraction in combination with liquid phase isomerization zone effluent produced as hereinafter described, fractionating said hydrocarbons to produce a substantially naphthene-free overhead hydrocarbon fraction and to produce a substantially pure cyclics hydrocarbon bottoms fraction containing methylcyclopentane and cyclohexane, removing said substantially pure methylcyclopentane and cyclohexane

hydrocarbon bottoms fraction as one product from the process, passing said substantially naphthene-free overhead hexane fraction from said first fractionation zone to a second fractionation zone as feed therefor, fractionating said hydrocarbons to produce an overhead hydrocarbon fraction containing 2,2- and 2,3-dimethylbutanes and to produce a bottoms hydrocarbon fraction containing methylpentanes and n-hexane, removing said overhead hydrocarbon fraction as a second product from the process, passing said last mentioned bottoms hydrocarbon fraction containing methylpentanes and n-hexane to an isomerization zone maintained at a temperature of from about 300° F. to about 800° F. and at a pressure of from about 100 to about 1000 pounds per square inch wherein methylpentanes and n-hexane are isomerized in the presence of said catalyst and hydrogen at a liquid hourly space velocity of from about 0.1 to about 10 to an equilibrium mixture of hexane hydrocarbons including 2,2- and 2,3-dimethylbutanes, recycling the isomerization zone effluent to the first mentioned fractionation zone as aforesaid to recover dimethylbutanes therefrom as one product and to separate methylpentanes and n-hexane as aforesaid for reuse and internal recycle in said process, and combining said second product with said cyclics hydrocarbon bottoms fraction to yield a hexane fraction having an F–1+3 octane number of at least 100.

4. The process of claim 3 further characterized in that the catalyst comprises alumina, from about 0.01% to about 2% by weight thereof of platinum, and from about 0.1% to about 8% by weight thereof of combined halogen.

5. The process of claim 4 further characterized in that the combined halogen is a mixture of chlorine and fluorine in an amount of from about 0.3% to about 0.7% by weight, and the isomerization is carried out at a temperature of from 750° to about 850° F.

6. The process of claim 4 further characterized in that the combined halogen is fluorine in an amount of from about 2.5% to about 4.5% by weight, and the isomerization is carried out at a temperature of from 500° to about 750° F.

7. The process of claim 4 further characterized in that the catalyst composite has impregnated thereon from about 5% to about 20% by weight of a Friedel-Crafts metal halide and the isomerization is carried out at a temperature of from 300° to about 500° F.

8. The process of claim 7 further characterized in that the Friedel-Crafts metal halide is aluminum chloride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,395,022	Sutton et al.	Feb. 19, 1946
2,440,751	Legatski	May 4, 1948
2,443,607	Evering	June 22, 1948
2,766,302	Elkins	Oct. 9, 1956
2,805,269	Carter et al.	Sept. 3, 1957
2,834,823	Patton et al.	May 13, 1958